

Circular dichroism in K -shell ionization from fixed-in-space CO and N_2

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We present results of calculations of the angular distributions of K -shell photoelectrons from fixed-in-space CO and N_2 molecules emitted by circularly polarized light. These calculated distributions account well for the strong circular dichroism recently reported in measurements of photoelectron distributions in these two systems. The calculations also serve to identify regions of photoelectron energy where pronounced circular dichroism can be expected in these spectra.

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In recent years there have been significant advances in the development of techniques for measuring angular distributions of photoelectrons as well as of ions from fixed-in-space molecules [1]. These measurements confirmed the rich dynamical structure of photoelectron angular distributions for fixed-in-space molecules first predicted in the seminal studies of Dehmer and Dill [2] some 25 years ago. Furthermore, recent theoretical studies employing Hartree-Fock and random-phase approximation (RPA) methods have yielded angular distributions in good agreement with measurements for fixed-in-space molecules, CO [3] and N_2 [4], respectively.

It was subsequently shown [5,6] that the photoelectron angular distributions from fixed-in-space linear molecules exhibit circular dichroism in the electric-dipole approximation (CDAD). Furthermore, explicit calculations for the 4σ level of CO also revealed the CDAD signal to be of the same magnitude as the angular distributions for right- and left-circularly polarized light [6]. While the first measurement of circular dichroism in the angular distributions of photoelectrons from the oxygen K shell of oriented CO were reported by Heiser *et al.* [7] in 1996 for a photon energy of 600 eV, Jahnke *et al.* [4] have recently measured the angular distributions of carbon K -shell photoelectrons for right- and left-circularly polarized light for oriented CO for electron energies of 1.6, 10.0, and 24.4 eV. Results were also reported for photoelectron energies of 2 and 9 eV for the K shell of N_2 [4]. These spectra, which exhibit a pronounced circular dichroism, can clearly provide benchmark tests for theoretical methods and models for calculating molecular photoelectron angular distributions.

In this paper, we report on results of calculations of the CDAD spectra for the carbon K shell of oriented CO and for the K shell of N_2 . The CDAD spectra were calculated within a relaxed-core Hartree-Fock (RCHF) approximation and employed a molecular basis set obtained using Slater's transition state approximation [8]. Cherepkov *et al.* [3] employed this same transition state potential in studies of K -shell ionization of CO. In this approximation, the relaxed molecular orbitals are derived from a self-consistent-field calculation with an average electron configuration where half electron is removed from the carbon K shell. This procedure attempts to capture some of the effects arising from screening of the hole in the K shell and, in fact, in the present studies locates the well-known σ shape resonances in CO and N_2 at photoelec-

tron energies of 8.5 and 9.0 eV, respectively, in good agreement with their measured positions [9]. To avoid working with nonorthogonal orbitals we also use this basis for the initial N -electron state and the final N -electron state with an electron in the continuum [10]. The photoelectron orbitals were obtained using an iterative procedure to solve the

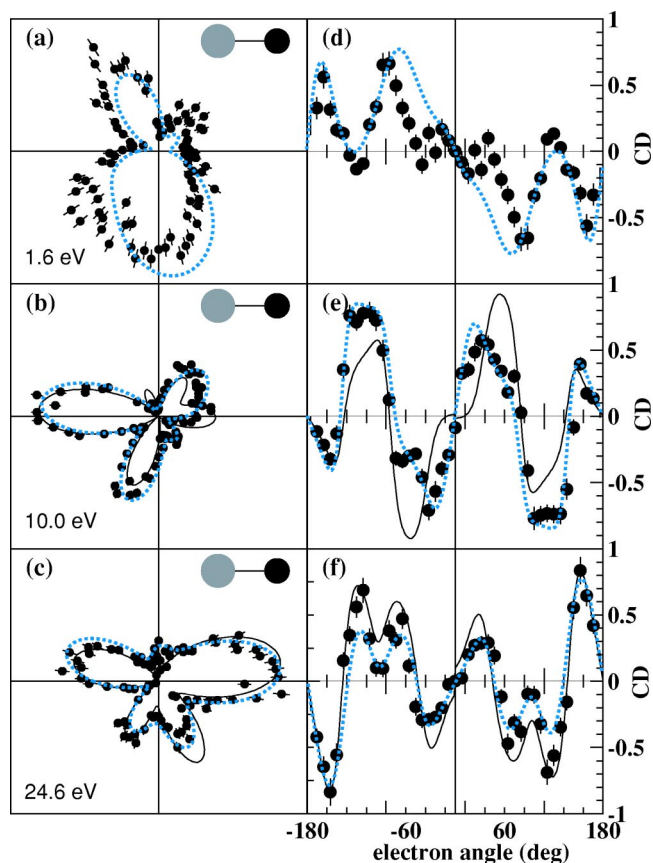


FIG. 1. Angular distributions for carbon K -shell photoelectrons emitted from a CO molecule by absorption of right-circularly polarized light propagating into the plane of the paper. The molecule lies along the horizontal axis as shown and electron detection is in the plane of the paper. Electron energies are 1.6, 10.0, and 24.6 eV in panels (a), (b), and (c), respectively. The corresponding CDAD spectra [see Eq. (1)] are shown in panels (d), (e), and (f). Electron angle 0 corresponds to the direction of the carbon: Dashed lines, present results; solid lines, multiple-scattering calculation [4].

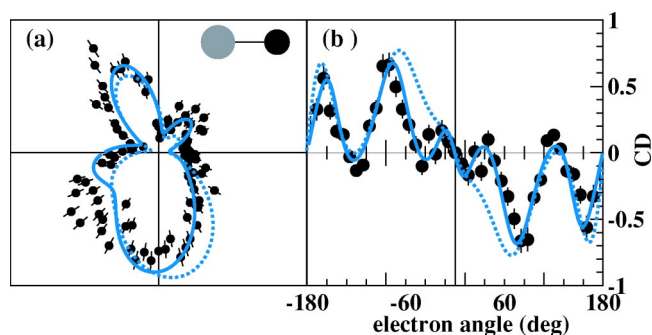


FIG. 2. The CDAD spectra for C 1s photoelectrons from CO (details as in Fig. 1). Filled circles: measured values of Ref. [4] at a photoelectron energy of 1.6 eV; solid (dashed) lines are the calculated CDAD spectra for a photoelectron energy of 3.6 eV (1.6 eV).

Lippmann-Schwinger equation associated with the one-electron Schrödinger equation which these orbitals satisfy [10].

Figure 1 compares our calculated angular distributions of carbon *K*-shell photoelectrons emitted from a fixed-in-space CO molecule by absorption of right-circularly polarized light and the corresponding CDAD spectra with the measured values of Jahnke *et al.* [4] at 1.6, 10.0, and 24.6 eV. The CDAD spectra are defined here as

$$S_{CDAD} = (\sigma_{LCP} - \sigma_{RCP}) / (\sigma_{LCP} + \sigma_{RCP}), \quad (1)$$

and are convoluted assuming a Gaussian detector function and the energy and angular resolutions given in Ref. [4]. The calculated angular distributions and CDAD spectra agree well with the measured values at 10.0 and 24.6 eV. The agreement, however, between the measured and calculated

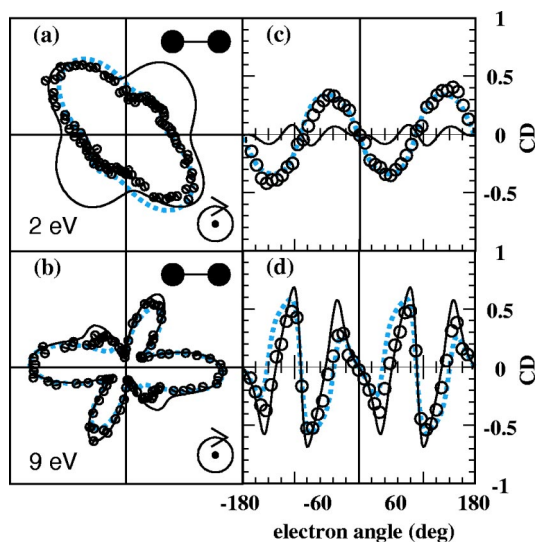


FIG. 3. Angular distributions for *K*-shell ionization of N_2 . The molecule lies along the horizontal axis and electron detection is in the plane of the paper. Photoelectron energy 2 eV (a), (c) and 9 eV (b), (d). (a) and (b) for left-circularly polarized light; (c) and (d), corresponding CDAD spectra. Dashed lines, present results; solid lines, RPA results [4]; circles, measurements [4].

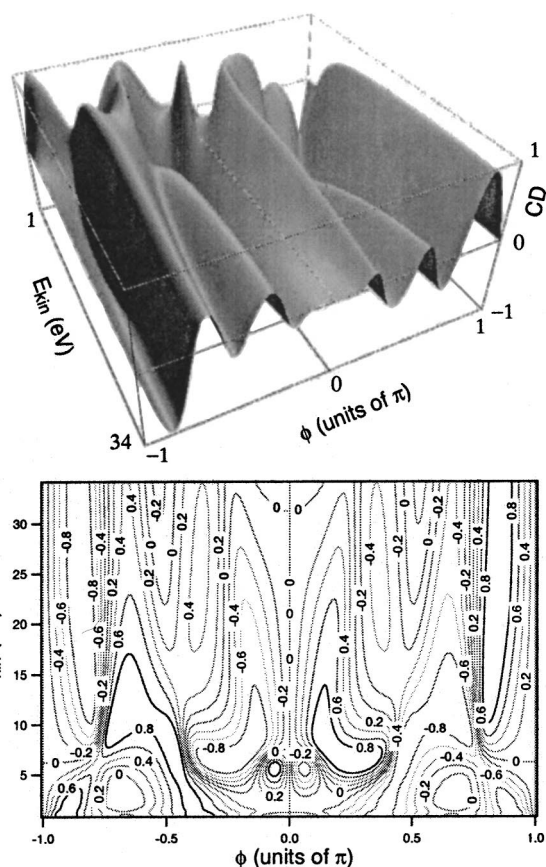


FIG. 4. Circular dichroism in the photoelectron angular distributions for the carbon *K* shell of CO. See caption of Fig. 1 for information on the plane of collection for the photoelectrons, direction of propagation of the light, and the orientation of the molecule. Electron angle $\phi = 0$ corresponds to the direction of the carbon. The data used for the three-dimensional plot at the top are shown as a contour plot at the bottom. These spectra are not convoluted.

spectra at the lowest energy of 1.6 eV is less satisfactory. While these differences could arise from shortcomings of the relaxed-core Hartree-Fock approximation employed in the calculations, it is interesting to compare the measured spectra at 1.6 eV with the calculated CDAD spectra at 3.6 eV (Fig. 2). The prominent structure around $\pm 40^\circ$ in the measured spectra at 1.6 eV is clearly not seen in the calculated spectra at this energy and only becomes apparent in the calculated spectra at higher photoelectron energies. Though this behavior may well be due to limitations of our calculations, it may also be suggestive of possible experimental issues.

Figure 1 also shows the calculated CDAD spectra of Ref. [4] for photoelectron energies of 10.0 and 24.6 eV. These spectra were calculated using a recent extension of multiple-scattering theory which includes regions of space neglected in standard multiple-scattering theory and avoids the usual spherical symmetrization of the potentials around each atomic scattering center. No spectra were reported for the lowest kinetic energy (1.6 eV) as the results at this energy were found to be too sensitive to a potential cutoff at long distances employed in this method [11].

Figure 3 compares our calculated angular distributions of

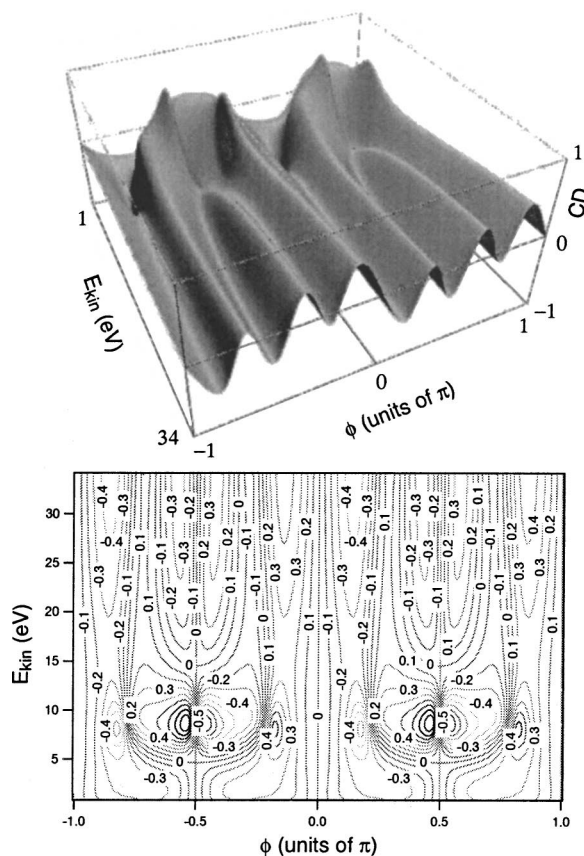


FIG. 5. Circular dichroism in the photoelectron angular distributions for the K shell of N_2 . See caption of Fig. 3 for information on the plane of collection for the photoelectrons, direction of propagation of the light, and the orientation of the molecule. The data used for the three-dimensional plot at the top are shown as a contour plot at the bottom. These spectra are not convoluted.

K -shell photoelectrons from a fixed-in-space N_2 molecule for absorption of left-circularly polarized light and the associated CDAD spectra with the measured values of Jahnke *et al.* [4] for photoelectron energies of 2 and 9 eV. These spectra are again convoluted assuming a Gaussian detector function and the energy and angular resolution cited in Ref. [4]. As in the case of CO, the molecule lies along the horizontal axis and electron detection is in the plane of the paper. With this geometry, the CDAD spectra are nonvanishing for a homonuclear diatomic molecule [6]. The calculated angular distributions for ionization by right-circularly polarized light and the CDAD spectra at 2 and 9 eV agree quite well with the measured spectra of Ref. [4]. Also shown for comparison in Fig. 3 are the results of RPA calculations reported in Ref. [4].

Finally, to highlight the dynamical behavior of these CDAD spectra, we show three-dimensional and contour plots of the circular dichroism in the K -shell angular distributions for CO and N_2 for a range of photoelectron energies in Figs. 4 and 5. These CDAD spectra exhibit a rich dynamical structure for photoelectron energies below around 10 eV. These regions may be well worth exploring in future measurements.

In conclusion, we have reported results of calculations of the angular distributions for K -shell photoelectrons from fixed-in-space CO and N_2 emitted by circularly polarized light. These calculated spectra, obtained by employing a relaxed-core Hartree-Fock model and Slater's transition state approximation, are seen to account nicely for the strong circular dichroism observed in recent measurements of these molecules [4].

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